

Atty. Docket #: 1998/F-101

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

INTERNATIONAL APPL. NO.: PCT/EP99/06324 :
INTERNATIONAL FILING DATE: -08/27/99- :
APPLICANT: DIRK VANDERZANDE ET AL :
SERIAL NO: : **ART UNIT:**
FILED: -HEREWITH- : **EXAMINER:**
FOR: PROCESS FOR THE PREPARATION :
OF DERIVATIVES OF :
4-ALKYLSULFINYLMETHYLARYLENEMETHANOL" :

Commissioner for Patents

Box PCT
Washington, D.C. 20231

"Express Mail" No.: EE617838545

Date: - MARCH 06, 2001 -

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- Valerie J. Murphy -
(Typed or printed name of mailing paper or fee)


(Signature of person mailing paper)

**TRANSMITTAL OF APPLICATION PAPERS
TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. §371
(37 CFR 1.494 OR 1.495)**

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. §371[f]) at any time rather than delay.
4. ☒ A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371[c](2)) --
a. ☒ is transmitted herewith (required when not transmitted by International Bureau).
b. ☐ has been transmitted by the International Bureau. See WIPO Publication WO
c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A (verified) translation of the International Application into the English language is enclosed.
7. ☐ Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371[c](3))
a. ☐ are transmitted herewith (required if not transmitted by the International Bureau).
b. ☐ have been transmitted by the International Bureau.
c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
d. ☐ have not been made and will not be made.
e. ☐ will be submitted with the appropriate surcharge.
8. ☐ A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371[c](3)) is enclosed or will be submitted with the appropriate surcharge.

International Application No. PCT/EP99/06324

1998/F-101

9. ☒ An oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371[c][4]) will follow.
☐ and is attached to the translation of (or a copy of) the International Application.
☐ and is attached to the substitute specification.

10. ☐ A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371[c][5]) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.
12. ☒ An Assignment for recording and a separate cover sheet in compliance with 37 CFR 3.28 and 3.31 will follow.
13. ☒ A FIRST preliminary amendment is enclosed.
A SECOND or SUBSEQUENT preliminary amendment is enclosed.
14. ☐ A substitute specification (including claims, abstract, drawing) is enclosed.
15. ☐ A change of power of attorney and/or address letter is enclosed.
16. ☒ Other items of information:

- ☒ This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of--

☐ 22 months from the priority date under 37 CFR 1.494(c), or

☒ 32 months from the priority date under 37 CFR 1.495(c).

- ☒ The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

International Application No. PCT/EP99/06324

1998/F-101

- ☒ Receiving Office: EPO
☒ IPEA (if filing under 37 CFR 1.495): EPO
☒ Priority Claim(s) (35 USC §§ 119, 365):
 German Appln. 198 40 943.5 filed -September 08, 1998-.
☒ A copy of the International Search Report is
 ☐ enclosed.
 ☒ attached to the copy of the International
 Application.
☒ A copy of the Receiving Office Request Form is enclosed.
☒ PCT/IB/308-1 sheet
☒ PCT/IB/306-1 sheet
☒ PTO/SB/05 -1 sheet

The fee calculation is set forth on the next page of this Transmittal Letter.

International Application No. PCT/EP99/06324

1998/F-101

FEE CALCULATION SHEET

☒ A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 860.00

Total Number of claims in
excess of (20) times \$18..... -0-

Number of independent claims
in excess of (3) times \$80..... -0-

Fee for multiple dependent
claims \$270..... -0-

TOTAL FILING FEE... \$ 860.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By 

DANIEL C. MULVENY

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DCM / des

Enclosures

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09/786581

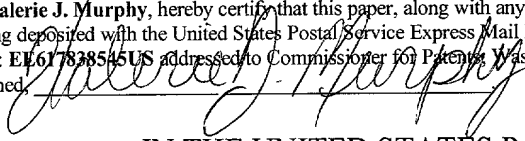
JC02 Rec'd PCT/PTO 05 MAR 2001

Attorney Docket No. 1998/F-101 US (8577*26)
PATENT

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Signed



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:)

Dirk VANDERZANDE et al.)

International Appl. No.: PCT/EP99/06324)

Group Art Unit:

International Filing Date: 27 August 1999)

Examiner:

Filed: 6 March 2001)

For: PROCESS FOR THE PREPARATION OF)
DERIVATIVES OF 4-ALKYLSULFINYL-)
METHYLARYLENEMETHANOL)

Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

In the above-captioned patent application, please amend the application as follows.

IN THE CLAIMS

Please cancel claims 2-17 without prejudice or disclaimer.

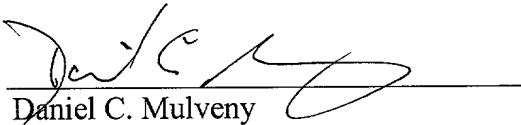
REMARKS

If any fees are due, please charge to Deposit Account No. 03-2775. Applicants believe no extension of time is required. Should the Examiner find otherwise, Applicants request such an extension of time be granted and the Commissioner is authorized to charge any deficiency in fees to Deposit Account No. 03-2775.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

Dated: 6 March 2001

By: 
Daniel C. Mulveny
Reg. No. 45,897

133675_1.DOC

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09/786581

JCO2 Rec'd PCT/PTO 05 MAR 2001

PROCESS
FOR THE
PREPARATION
OF
DERIVATIVES
OF
4-ALKYLSULFINYLMETHYLARYLENEMETHANOL

Dirk Vanderzande
Joanes Gelan
Albert Van Breemen
Michael Van Der Borght
Laurence Lutsen
Raf Kiebooms
-and-
Willi Kreuder

TRANSLATION
OF
INTERNATIONAL APPLICATION

PCT/EP99/06324 IFD: 08/27/1999

1998/F-101 (8577*26)

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09786581-000004

Process for the preparation of derivatives of 4-alkylsulfinylmethylarylene-methanol

5

The present invention relates to a process for the preparation of derivatives of 4-alkylsulfinylmethylarylenemethanol. Derivatives of 4-alkylsulfinylmethylarylenemethanol are valuable monomers in the preparation of conjugated polymers, which are suitable, inter alia, as electroluminescent materials.

10

There is considerable industrial demand for large-area solid-state light sources for a number of applications, predominantly in the area of display elements, display-screen technology and illumination technology. The requirements made of these light sources cannot at present be completely satisfied by any of the existing technologies.

15

As an alternative to conventional display and illumination elements, such as incandescent lamps, gas-discharge lamps and non-self-illuminating liquid-crystal display elements, electroluminescent (EL) materials and devices, such as light-emitting diodes (LEDs), have already been in use for some time.

20

Besides inorganic electroluminescent materials and devices, low-molecular-weight, organic electroluminescent materials and devices have also been known for about 30 years (see, for example, US-A-3,172,862). Until recently, however, such devices were greatly limited in their practical applicability.

25

EP-A-0 423 283 and EP-A-0 443 861 describe electroluminescent devices which contain a film of a conjugated polymer as light-emitting layer (semiconductor layer). Such devices offer numerous advantages, such as the possibility of manufacturing large-area, flexible displays simply and inexpensively. In contrast to liquid-crystal displays, electroluminescent displays are self-illuminating and therefore do not require an additional illumination source at the back.

30

35

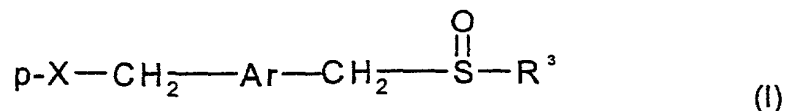
5 A typical device in accordance with EP-A-0 423 283 consists of a light-emitting layer in the form of a thin, dense polymer film (semiconductor layer) containing at least one conjugated polymer. A first contact layer is in contact with a first surface, and a second contact layer is in contact with a further surface of the semiconductor layer. The polymer film of the semiconductor layer has a sufficiently low concentration of extrinsic charge carriers so that, on application of an electric field between the two contact layers, charge carriers are introduced into the semiconductor layer, the first contact layer becoming positive compared with the other layer, and the semiconductor layer emits radiation. The polymers used in such devices are conjugated. The term "conjugated polymer" is taken to mean a polymer which has a delocalized electron system along the main chain. The delocalized electron system gives the polymer semiconductor properties and enables it to transport positive and/or negative charge carriers with high mobility.

10 EP-A-0 423 283 and EP-A-0 443 861 describe poly(p-phenylenevinylene) as polymeric material for the light-emitting layer. This can be modified by alkyl, alkoxy, halogen or nitro substituents on the aromatic ring. Such polymers have since then been investigated in a large number of studies, and dialkoxy-substituted PPVs in particular have already been optimized to a considerable extent toward the market introduction stage (cf., for example, J. Salbeck, Ber. Bunsenges. Phys. Chem. 1996, 100, 1667). However, the development of such polymers can in no way be regarded as complete. Thus, inter alia, improvements are still necessary regarding the service life, stability and also the achievable color. For example, the above polymer class which has been developed the furthest, dialkoxy-PPVs, is only suitable for emission of orange-red light.

20 30 The above polymers require on the one hand high-purity monomers and also very complex monomers. Some of these monomers units are only accessible in the requisite quality by complex methods and must furthermore be purified by chromatography after their complex preparation.

35 There is therefore a great demand for processes for the preparation of corresponding monomer units in which the monomers are obtained in such a quality that chromatographic purification is unnecessary.

The present invention relates to a process for the preparation of compounds of the formula (I)



in which

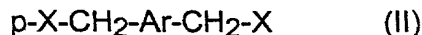
Ar is an aromatic ring system having 4 to 20 carbon atoms, which may, if desired, be monosubstituted or polysubstituted by C₁-C₂₀-alkyl, C₃-C₂₀-alkoxy, C₃-C₂₀-branched alkyl, phenyl or benzyl radicals and which may contain up to 4 heteroatoms from the group consisting of oxygen, sulfur and nitrogen in the aromatic ring system,

X is a leaving group, and

R³ is unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl, such as cyclohexyl, or C₁-C₄-alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, phenyl or benzyl, which may be substituted or unsubstituted and/or contain heteroatoms, such as O, N and Si,

comprising the following measures:

a) reaction of a compound of the formula (II)

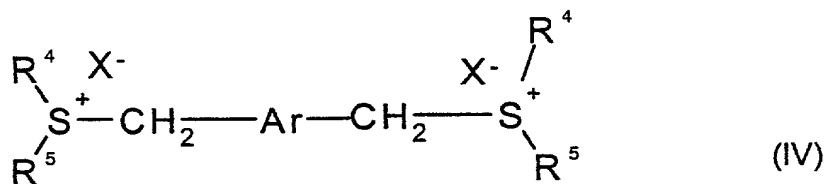


in which Ar and X are as defined under the formula (I), with an organic sulfide of the formula (III)



in which

R⁴ and R⁵ are identical or different and are unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl having 3 to 10 carbon atoms, such as cyclobutyl, cyclopentyl or cyclohexyl, or C₁-C₄-alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, or R⁴ and R⁵ together form a ring, which may also contain one or more heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen, to give a compound of the formula (IV)



in which R^4 , R^5 , X and Ar are as defined above,

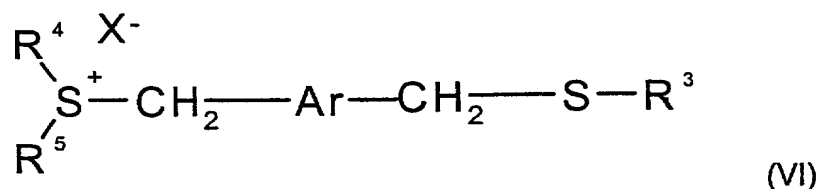
- b) reaction of the compound of the formula (IV) with from 0.85 to 1.1 equivalents of a mercaptan of the formula (V)



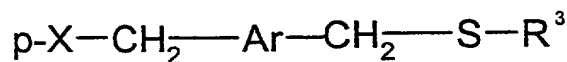
in which

R^3 is unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl, such as cyclohexyl, or C_1 - C_4 -alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, phenyl or benzyl, which may be substituted or unsubstituted and/or contain heteroatoms, such as O, N and Si,

to give a compound of the formula (VI)



- c) warming of the compound of the formula (VI) in a liquid and formation of the compound of the formula (VII)



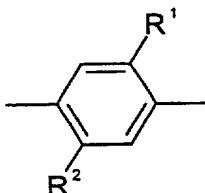
by elimination of an organic sulfide of the formula (III), where the compound of the formula (VII) is dissolved in the above liquid,

- d) oxidation of the compound of the formula (VII) using an oxidant, to give the compound of the formula (I).

The radical X is preferably a leaving group, such as halogen, -O-tosylate, -O-mesylate or -O-trifluoroacetate.

In the formula (I), p denotes para in respect of the two methylene radicals -CH₂- on both sides of the radical Ar.

The process according to the invention is preferably used for the preparation of compounds of the formula (I) in which Ar is the structural unit



in which

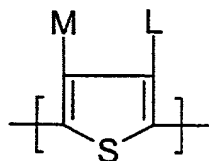
R¹ and R² are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 20 carbon atoms, a branched alkyl or alkoxy radical having 3 to 20 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted by halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 20 carbon atoms.

Particular preference is given to compounds of the formula (I) in which Ar is as defined above, and R¹ and R², independently of one another, are an unbranched alkoxy radical having 1 to 20 carbon atoms, a branched alkoxy radical having 3 to 20 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted by halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 20 carbon atoms.

Preference is furthermore given to compounds of the formula (I) in which R¹ and R², independently of one another, are an unbranched alkoxy radical having 1 to 10 carbon atoms, a branched alkoxy radical having 3 to 20 carbon atoms, or phenyl, which may be substituted by one or more branched or unbranched alkyl or alkoxy groups having up to 20 carbon atoms.

R³ is preferably n-, i-, s- or t-butyl, i-pentyl, octyl, 3,6,9-trioxadecyl, 2-hydroxyethyl or 2-chloroethyl, particularly n-butyl or n-octyl.

The process according to the invention is equally preferably used for the preparation of compounds of the formula (I) in which Ar is the structural unit



in which

M and L are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 16 carbon atoms, a branched alkyl or alkoxy radical having 3 to 16 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted by halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 16 carbon atoms, or M and L together are a bridge having at least 4 bridge members, which may also contain one or more heteroatoms, in particular oxygen and/or sulfur.

The reaction of the compound of the formula (II) with a sulfide of the formula (III) with formation of the bissulfonium salt of the formula (IV) is described, for example, in P.L.Burn, D.D.Bradley, R.H. Friend, D.A.Halliday, A.B.Holmes, J.Chem.Soc.Perkin Trans. 1,23,1992, 3225; P.L. Burn et al., J.Amer.Chem.Soc., 115, 22, 1993, 10117; Lee et al., Mol.Cryst.Liq.Cryst.Sci.Technol.Sect.A, 247, 1994, 121; D. Hwang, J.Chem.Soc.Chem.Comm. 21,1994, 2461; J. Jin et al., J.Chem.Soc.Chem.Comm. 17,1989, 1205; J.D. Stenger-Smith et al., J.Org.Chem. 59, 20,1994, 6107; Hwang, C. Yoon, K. Moon, H. Shim, Mol.Cryst.Liq.Cryst.Sci.Technol.Sect.A, 280, 1996, 39 and 175 and 181; A. Luettringhaus, H. Machatzke, Arzneimittel Forsch. 13, 1963, 366; Bardsley, Ashford, Biochem. J. 128, 1972, 253-6; Luettringhaus, H. Machatzke, Justus Liebigs Ann.Chem. 671, 1964, 165-196; G.M. Brooke, S.D. Mawson, J.Fluorine Chem. 50, 1, 1990, 101; S. Antoun, Collect.Czech.Chem.Comm. 52, 1, 1987, 162; and Y. Sonoda, K. Kaeriyama, Bull.Chem.Soc.Jpn. 65, 3, 1992, 853.

The organic sulfide of the formula (III) is preferably dimethyl sulfide, diethyl sulfide, 2-ethylthioethanol, thiobisethanol, or a cyclic sulfide, such as tetrahydrothiopyran (= pentamethylene sulfide) or tetrahydrothiophene (THT). Particular preference is given to tetrahydrothiophene (THT).

The reaction is usually carried out in solvents, such as methanol, water, ethanol, acetone, dioxane, tetrahydropyran, tetrahydrofuran or acetonitrile, mixtures frequently also being advantageous, at temperatures between room temperature (20°C) and the boiling point of the mixture (about 100°C), preferably between 20° and 60°C.

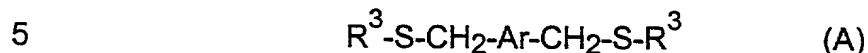
From 2 to 8 equivalents of the sulfide of the formula (III) are employed per mole of the starting compound of the formula (II). About 5 equivalents are preferably employed. In the subsequent reaction step (b), the bissulfonium salt of the formula (IV) is reacted with a mercaptan of the formula (V).

The reaction is carried out in the presence of a base, where from 0.85 to 1.1 equivalents, in particular from 0.9 to 1.05 equivalents, of base are added per mole of bissulfonium salt. Suitable bases are inorganic and organic bases. Suitable inorganic bases are NaOH, KOH and LiOH. Suitable organic bases are, in particular, sterically hindered bases, such as lithium diisopropylamide (LDA), sodium trimethylsilanoate, bis(trimethylsilyl)potassium amide, but in particular alkali metal tert-butoxides, such as KOtBu and NaOtBu.

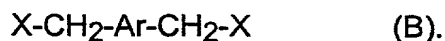
From 0.85 to 1.1 equivalents, in particular from 0.95 to 1.05 equivalents, of mercaptan of the formula (V) are employed per mole of bissulfonium salt of the formula (IV). The reaction is advantageously carried out at temperatures of between 0° and 40°C, particularly preferably at below room temperature (about 10°C). The reaction is carried out in the presence of a polar, protic solvent. Suitable solvents are ethanol, n- and i-propanol, n-, i-, sec- and tert-butanol and mixtures, in particular methanol.

The reaction mixture is subsequently neutralized, concentrated, if necessary freed from solid and diluted with a non-polar, aprotic organic solvent whose boiling point is above that of the abovementioned polar, protic solvent. The relatively low-boiling fraction comprising polar, protic solvent and sulfide is subsequently removed, for example by evaporation under reduced pressure or by other suitable measures. By repeating this operation, the sulfide of the formula (III) is removed from the equilibrium and replaced by the leaving group X.

The concentrated solution which remains also contains, besides the compound of the formula (VI), the two possible by-products of the formula (A)



and of the formula (B)



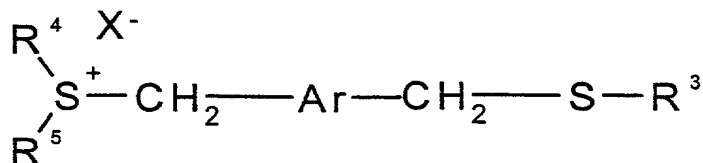
Surprisingly, the proportion of by-products of the formulae (A) and (B) is not as expected 25% of theory each, but is significantly lower. The detected proportion of compounds of the formulae (A) and (B) is, surprisingly, less than 15% and frequently only 5%.

The compound of the formula (VII) obtained in this way is subsequently oxidized to the sulfoxide by methods known from the literature (J. March, Adv. Org. Chem., 3rd Edn., J. Wiley, New York, pp. 1089-90).

Preference is given to a catalytic oxidation using peroxides, in particular hydrogen peroxide. Examples of suitable catalysts are SeO_2 and TeO_2 . Air or oxygen can also advantageously be employed with catalytic amounts of NO_2 .

The target compound of the formula (I) can advantageously be isolated by recrystallization from low-boiling solvents, such as alkanes, alcohols, ketones, ethers or esters. Complex chromatographic purification is unnecessary owing to the high selectivity of the process according to the invention.

The present invention furthermore relates to the compounds of the formula (VI)



in which Ar, R^3 , R^4 , R^5 and X are as defined above.

The compounds of the formula (VI) are valuable intermediates in the synthesis of compounds of the formula (I) and can be isolated if desired.

5 Examples

Example 1: p-Xylylenebis(tetrahydrothiophenium chloride)

A solution of 52.5 g (0.3 mol) of p-xylylene dichloride in 105 ml (1.19 mol) of tetrahydrothiophene and 105 ml of methanol was stirred for 60 hours at room temperature. The reaction mixture was stirred into 420 ml of acetone at -10°C. The hygroscopic precipitate was rinsed with 600 ml of cold acetone and dried. 95.9 g, 91 %.

Example 2: p-(Octylthiomethyl)benzyl chloride

1.83 g (19 mmol) of sodium t-butoxide and 2.78 g (19 mmol) of octanethiol were stirred into 40 g of methanol at room temperature. After 30 minutes, the clear solution was added in one portion to 6.68 g (19 mmol) of the p-xylylenebis(tetrahydrothiophenium chloride) obtained in accordance with Example 1, in 100 g of methanol. After one hour, the mixture was neutralized using 1N hydrochloric acid, and all the volatile components were removed under reduced pressure. The crude product was taken up in 200 ml of chloroform, the undissolved constituents were filtered off, and the filtrate was evaporated under reduced pressure. The oil was mixed with twice the volume of octane, and distilled off under reduced pressure together with tetrahydrothiophene. This sequence was repeated three times with octane, finally giving 5.31 g, consisting of 90% of product, 5% of starting material and 5% of p-bis(octylthiomethyl)benzene. This reaction was carried out at various temperatures and the product distribution analyzed by ¹H-NMR spectroscopy (all data in mol-%).

Temp./°C	Starting material	Product	p-Bis(octylthiomethyl)-benzene
-20	8	84	8
0	6	87	7
20	5	90	5
40	6	87	7

Repetition of the experiments at 20°C, but with a slightly less than the stoichiometric amount of the mercaptan, gave the following product distribution:

RSH equivalents	Starting material	Product	p-Bis(octylthiomethyl)- benzene
0.95	14	78	8
0.98	8	84	8
1.00	5	90	5

Comparative Example A: p-(Octylthiomethyl)benzyl chloride

A solution of 14.3 g (0.10 mol) of octanethiol in 100 ml of toluene was added dropwise at room temperature over the course of 24 hours to a stirred mixture of 39.4 g (0.225 mol) of p-xylylene dichloride in 400 ml of toluene, 23.7 g (0.59 mol) of NaOH in 400 ml of water and 1 g of Aliquat 336 as phase-transfer catalyst. The separated-off organic layer was washed three times with 200 ml of water each time, dried and evaporated under reduced pressure. 32.0 g, which, according to $^1\text{H-NMR}$ spectroscopy, consisted of 39% of product, 59% of starting material and 2% of p-bis(octylthiomethyl)benzene.

Repetition of the experiment, but without an excess of the p-xylylene dichloride, gave the following product distribution:

RSH equivalents	Starting material	Product	p-Bis(octylthiomethyl)- benzene
1.00	19-25	50-63	18-25
0.45	70	28	2

Comparative Example B: p-(Octylthiomethyl)benzyl chloride

1.83 g (19 mmol) of sodium t-butoxide and 2.78 g (19 mmol) of octanethiol were stirred into 40 g of methanol at room temperature. After 30 minutes, the clear solution was added in one portion to 3.33 g (19 mmol) of p-xylylene dichloride in 100 g of methanol. After one hour, the mixture was neutralized using 1N hydrochloric acid, and all the volatile components were removed under reduced pressure. The crude product was taken up in 250 ml of chloroform and washed twice with 100 ml of water each time,

dried and evaporated under reduced pressure. 5.29 g, which, according to ^1H -NMR-spectroscopy, consisted of 50% of product, 25% of starting material and 25% of p-bis(octylthiomethyl)benzene.

5 Example 3: p-(Butylsulfinylmethyl)benzyl chloride

A solution of 17.1 g (178 mmol) of sodium t-butoxide and 19.4 ml (16.4 g, 181 mmol) of butanethiol in methanol was added to a clear solution of 67.1 g of the bissulfonium salt prepared in accordance with Example 1 in 300 ml of methanol. After 30 minutes, the solvent was removed, and octane was added and distilled off. This last sequence was repeated three times. The oil which remained was taken up in chloroform, washed with water and sodium hydrogencarbonate solution, dried over magnesium sulfate and filtered, which also removed undissolved organic residues. Hydrogen peroxide was added to a solution of this intermediate in 50 ml of 1,4-dioxane, 250 ml of methanol and tellurium dioxide. After five hours, 100 ml of saturated sodium chloride solution were added, and the mixture was extracted with chloroform and dried, giving 43.4 g of p-(butylsulfinylmethyl)benzyl chloride.

Recrystallization from 800 ml of acetone followed by crystallization from chloroform/hexane gave 40 g of the product in extremely high purity. ^1H -NMR spectroscopy only showed impurities at the level of ^{13}C satellites.

Example 4:

2-(3,7-Dimethyloctyloxy)-5-methoxyxylylene-1,4-bis(tetrahydrothiophenium chloride)

10 g (27.7 mmol) of 1,4-bischloromethyl-2-(3,7-dimethyloctyloxy)-5-methoxybenzene (BCDM) and 12.4 g (141 mmol) of tetrahydrothiophene (THT) were dissolved in 20 ml of methanol at 30°C. After 70 hours, excess THT was distilled off, and the residue was dissolved in just sufficient methanol, filtered and stirred into 100 ml of ice-cold acetone. The solid was digested with 40 ml of hexane. Drying for 4 hours under reduced pressure gave 11 g (72 % of theory).

Example 5:

2-(3,7-Dimethyloctyloxy)-5-methoxy-4-butylthiomethylbenzyl chloride via 2-(3,7-dimethyloctyloxy)-5-methoxy-4-butylthiomethylbenzyl tetrahydrothiophenium chloride, each as a mixture of the regioisomers

6.5 g (68 mmol) of sodium t-butoxide (1 eq.) and 6.0 g (66.5 mmol, 0.98 eq.) of butanethiol (BuSH) were stirred into 150 ml of methanol at 20°C. After 30 minutes, the clear solution was added dropwise to a solution of 37.6 g (68 mmol, 1 eq.) of the salt prepared in accordance with Example 4 in 400 ml of methanol. After a reaction time of 60 minutes at 20°C, the mixture was neutralized using 1N hydrochloric acid, after which all the volatile components were distilled off under reduced pressure. The residue was taken up in 200 ml of chloroform and filtered. The filtrate was concentrated under reduced pressure, and the resultant oil was taken up in 80 ml. After the mixture of octane and THT had been evaporated, this procedure was repeated three times. Yield 39.5 g, consisting of 18% of BCDM, 7% of bisthioether and 74% of the desired product as a 50:50 mixture of the two regioisomers 2-(3,7-dimethyloctyloxy)-5-methoxy-4-butylthiomethylbenzyl chloride and 5-(3,7-dimethyloctyloxy)-2-methoxy-4-butylthiomethylbenzyl chloride. The two regioisomers were also isolated by preparative column chromatography.

Example 6:

Example 5 was repeated with the following modifications:

- reaction time of 40 instead of 60 minutes
- 1.1 equivalents of NaOtBu instead of 1 eq.
- 0.99 equivalent of BuSH instead of 0.98 eq.

16% of BCDM, 7% of bisthioether and 77% of the desired product as a 49:51 mixture of the two regioisomers, and slight traces of the polymer undesired here, were obtained.

Example 7:

39.5 g of the product from Example 5 were dissolved in 200 ml of dioxane, and 1.82 g (11.4 mmol, 12 mol-%) of tellurium dioxide were added. 18.5 g (190 mmol) of a 35 % strength aqueous hydrogen peroxide solution were added dropwise at room temperature with vigorous stirring. As soon as a trace of the sulfone, as a sign of overoxidation, was detectable by thin layer chromatography, (3.5 hours), the reaction was terminated by pouring in ice-water. The aqueous phase was extracted with three portions of chloroform (250, 100 and 100 ml). After drying, the combined organic phases gave 30 g of the product: 76% of the desired regioisomer 2-(3,7-dimethyloctyloxy)-5-methoxy-4-butylsulfinylmethylbenzyl chloride and 5-(3,7-dimethyl-

octyloxy)-2-methoxy-4-butylsulfinylmethylbenzyl chloride, 16% of BCDM and 7% of the bis(butylsulfinyl) derivative.

5 This mixture can successfully be employed for polymerization even without purification.

Example 8:

Example 5 was repeated with the reaction temperature lowered from 20° to 10° or 0°C. The following product distribution was found:

10

Temp./°C	BCDM	Bisbutylthio derivative	Product (regioisomers)
20	18	7	74 (50:50)
10	19	4	77 (51:49)
0	17	4	79 (51:49)

Example 9:

2,5-Dimethylylene dichloride (9a),
2,5-dimethoxyxylylene dichloride (9b) and
15 2,5-dichloroxylylene dichloride (9c)

were prepared in accordance with Example 5, where, owing to the improved solubility, methanol or mixtures with water were selected as solvent in the reaction with BuSH:

20

Example	MeOH:H ₂ O	Starting material	Product	Bis(butylthio)xylene derivative
9a	1:0	9	86	5
9b	1:0	8	80	12
9c	4:1	7	86	7

4-Butylthiomethyl-2,5-dicyanobenzyl chloride can be prepared in an analogous manner in acetonitrile:water (65:35). 2-Butylthiomethyl-2-chloro-methylnaphthalene was obtained in anhydrous methanol.

25

Comparative Experiment: p-Phenylsulfinylmethylbenzyl chloride

3.8 ml (37.8 mmol) of thiophenol were dissolved in 100 ml of dry tetrahydrofuran (THF), and 0.91 g (37.8 mmol) of NaH were slowly added. The suspension was added dropwise to a vigorously stirred solution, at

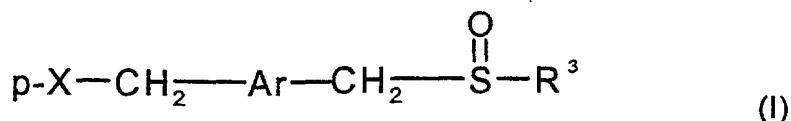
25°C, of 33.08 g (189 mmol, i.e. a five-fold excess) of p-bischloromethylbenzene in 150 ml. After 14 hours, 100 ml of water were added, and the mixture was extracted four times with 50 ml of chloroform each time. The combined organic extracts were dried over magnesium sulfate, and the solvent was evaporated, ultimately under reduced pressure.

The crude mixture, consisting of p-bischloromethylbenzene, p-(bisphenylthiomethyl)benzene and the desired p-phenylthiomethylbenzyl chloride, was subjected, without further purification, to oxidation to the sulfoxide:

The mixture was dissolved in 450 ml of methanol together with 0.6 g (0.037 mmol) of TeO_2 . 8.6 ml of 30% strength by weight hydrogen peroxide (76 mmol) were added dropwise with vigorous stirring. 4 hours later, 100 ml of water were added, the aqueous phase was extracted with chloroform, dried as usual using magnesium sulfate and evaporated to dryness. The crude product (30 g) was purified by chromatography over silica gel (300 g). After recrystallization from hexane/toluene, 5.5 g of p-phenylsulfinylmethylbenzyl chloride were obtained as colorless crystals. The yield is 55% based on thiophenol, but only 11% based on the bischloromethyl compound (5-fold excess).

Patent claims

1. A process for the preparation of compounds of the formula (I)



in which

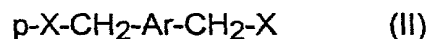
Ar is an aromatic ring system having 4 to 20 carbon atoms, which may, if desired, be monosubstituted or polysubstituted by C₁-C₂₀-alkyl, C₃-C₂₀-alkoxy, C₃-C₂₀-branched alkyl, phenyl or benzyl radicals and which may contain up to 4 heteroatoms from the group consisting of oxygen, sulfur and nitrogen in the aromatic ring system,

X is a leaving group, and

R³ is unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl, such as cyclohexyl, or C₁-C₄-alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, phenyl or benzyl, which may be substituted or unsubstituted and/or contain heteroatoms, such as O, N and Si,

comprising the following measures:

- a) reaction of a compound of the formula (II)



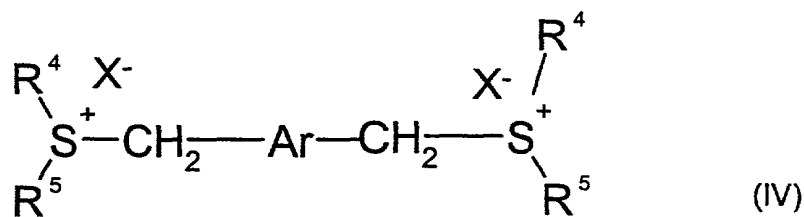
in which Ar and X are as defined under the formula (I), with an organic sulfide of the formula (III)



in which

R⁴ and R⁵ are identical or different and are unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl having 3 to 10 carbon atoms, such as cyclobutyl, cyclopentyl or cyclohexyl, or C₁-C₄-alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, or R⁴ and R⁵ together form a ring, which may also contain one or more heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen,

to give a compound of the formula (IV)



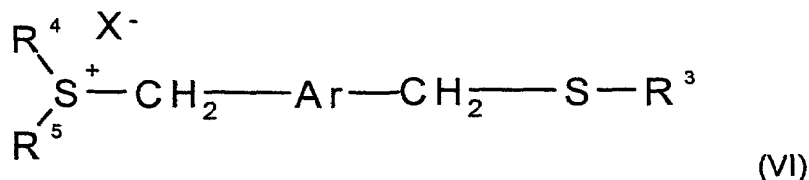
- 5 in which R^4 , R^5 , X and Ar are as defined above,
 b) reaction of the compound of the formula (IV) with from 0.85 to 1.1 equivalents of a mercaptan of the formula (V)



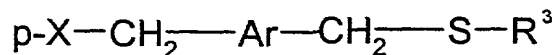
in which

R^3 is unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl, such as cyclohexyl, or C_1 - C_4 -alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, phenyl or benzyl, which may be substituted or unsubstituted and/or contain heteroatoms, such as O, N and Si,

to give a compound of the formula (VI)



- c) warming of the compound of the formula (VI) in a liquid and formation of the compound of the formula (VII)

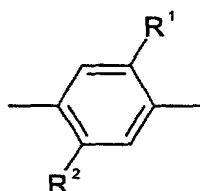


by elimination of an organic sulfide of the formula (III), where the compound of the formula (VII) is dissolved in the above liquid,

- d) oxidation of the compound of the formula (VII) using an oxidant, to give the compound of the formula (I).

2. The process as claimed in claim 1, wherein the radical X is a leaving group, such as halogen, -O-tosylate, -O-mesylate or -O-trifluoroacetate.

3. The process as claimed in claim 1 or 2, wherein Ar is the structural unit

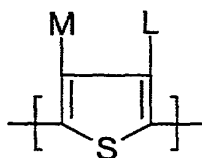


in which

10 R¹ and R² are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 20 carbon atoms, a branched alkyl or alkoxy radical having 3 to 20 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted by halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or

15 an ester having 1 to 20 carbon atoms.

4. The process as claimed in one of claims 1 to 3, wherein Ar is the structural unit



in which

20 M and L are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 16 carbon atoms, a branched alkyl or alkoxy radical having 3 to 16 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted by halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or

25 an ester having 1 to 16 carbon atoms, or M and L together are a bridge having at least 4 bridge members, which may also contain

30 one or more heteroatoms, in particular oxygen and/or sulfur.

5. The process as claimed in claim 3, wherein R^1 and R^2 , independently of one another, are an unbranched alkoxy radical having 1 to 20 carbon atoms, a branched alkoxy radical having 3 to 20 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted by halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 20 carbon atoms.

6. The process as claimed in claim 5, wherein R^1 and R^2 , independently of one another, are an unbranched alkoxy radical having 1 to 10 carbon atoms, a branched alkoxy radical having 3 to 20 carbon atoms, or phenyl, which may be substituted by one or more branched or unbranched alkyl or alkoxy groups having up to 20 carbon atoms.

7. The process as claimed in one of claims 1 to 6, wherein R^3 is n-, i-, s- or t-butyl, i-pentyl, octyl, 3,6,9-trioxadecyl, 2-hydroxyethyl or 2-chloroethyl.

8. The process as claimed in one of claims 1 to 7, wherein the organic sulfide of the formula (III) is dimethyl sulfide, diethyl sulfide, 2-ethylthioethanol, thiobisethanol, or a cyclic sulfide, in particular tetrahydrothiopyran (= pentamethylene sulfide) or tetrahydrothiophene (THT).

9. The process as claimed in one of claims 1 to 8, wherein the reaction in measure (a) is carried out in methanol, water, ethanol, acetone, dioxane, tetrahydropyran, tetrahydrofuran, acetonitrile or mixtures thereof.

10. The process as claimed in one of claims 1 to 9, wherein the reaction in measure (a) is carried out at temperatures between room temperature (20°C) and the boiling point of the mixture (100°C).

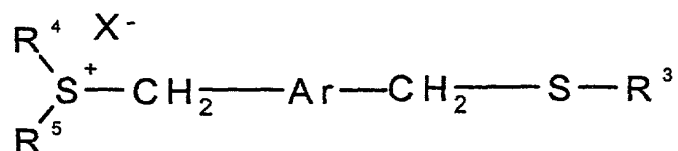
11. The process as claimed in one of claims 1 to 10, wherein the reaction in measure (b) is carried out in the presence of a base.

12. The process as claimed in one of claims 1 to 11, wherein from 0.95 to 1.05 equivalents of mercaptan of the formula (V) are employed per mole of the compound of the formula (IV).

13. The process as claimed in one of claims 1 to 12, wherein the reaction in measure (b) is carried out at between 0°C and 40°C.

14. The process as claimed in one of claims 1 to 13, wherein the reaction in measure (b) is carried out in a polar, protic solvent.

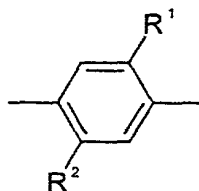
5 15. A compound of the formula (VI)



in which

- 10 Ar is an aromatic ring system having 4 to 20 carbon atoms, which may, if desired, be monosubstituted or polysubstituted by C₁-C₂₀-alkyl, C₃-C₂₀-alkoxy, C₃-C₂₀-branched alkyl, phenyl or benzyl radicals and which may contain up to 4 heteroatoms from the group consisting of oxygen, sulfur and nitrogen in the aromatic ring system,
- 15 X is a leaving group, and R³ is unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl, such as cyclohexyl, or C₁-C₄-alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, phenyl or benzyl, which may be substituted or unsubstituted and/or
- 20 contain heteroatoms, such as O, N or Si, R⁴ and R⁵ are identical or different and are unbranched alkyl having 1 to 20 carbon atoms, branched alkyl having 3 to 20 carbon atoms, cyclic alkyl having 3 to 10 carbon atoms, such as cyclobutyl, cyclopentyl or cyclohexyl, or C₁-C₄-alkyl-substituted cyclic alkyl, such as cyclohexylmethyl, or R⁴ and R⁵ together form a ring, which may also
- 25 contain one or more heteroatoms selected from the group consisting of oxygen, sulfur and nitrogen.

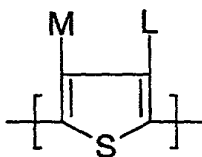
30 16. A compound as claimed in claim 15, wherein Ar is the structural unit



in which

R^1 and R^2 are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 20 carbon atoms, a branched alkyl or alkoxy radical having 3 to 20 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted by halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 20 carbon atoms.

17. A compound as claimed in claim 15, wherein Ar is the structural unit



in which

M and L are identical or different and are hydrogen, an unbranched alkyl or alkoxy radical having 1 to 16 carbon atoms, a branched alkyl or alkoxy radical having 3 to 16 carbon atoms, phenyl or benzyl, where the abovementioned radicals may be unsubstituted or substituted by halogen, in particular chlorine, bromine or fluorine, cyano, nitro, or an ester having 1 to 16 carbon atoms, or M and L together are a bridge having at least 4 bridge members, which may also contain one or more heteroatoms, in particular oxygen and/or sulfur.

Variable	Mean	SD	Min	Max	Skewness	Kurtosis	Normality
Age	35.2	12.5	18	65	0.15	3.2	0.98
Gender	0.55	0.50	0	1	-0.05	3.0	0.99
Marital Status	0.65	0.48	0	1	0.10	3.1	0.99
Education	12.5	2.5	9	16	-0.20	3.3	0.97
Income	45000	15000	20000	80000	0.30	3.4	0.96
Health	0.75	0.43	0	1	-0.10	3.0	0.99
Stress	0.60	0.49	0	1	0.05	3.1	0.99
Depression	0.50	0.50	0	1	-0.05	3.0	0.99
Life Satisfaction	0.70	0.46	0	1	-0.15	3.2	0.98
Resilience	0.65	0.47	0	1	0.00	3.1	0.99
Optimism	0.70	0.45	0	1	-0.10	3.2	0.98
Gratitude	0.60	0.48	0	1	0.05	3.1	0.99
Self-Compassion	0.55	0.49	0	1	-0.05	3.0	0.99
Emotional Regulation	0.65	0.47	0	1	0.00	3.1	0.99
Psychological Well-being	0.75	0.43	0	1	-0.10	3.2	0.98
Life Satisfaction	0.70	0.45	0	1	-0.15	3.2	0.98
Resilience	0.65	0.47	0	1	0.00	3.1	0.99
Optimism	0.70	0.45	0	1	-0.10	3.2	0.98
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Self-Compassion	0.55	0.49	0	1	-0.05	3.0	0.99
Emotional Regulation	0.65	0.47	0	1	0.00	3.1	0.99
Psychological Well-being	0.75	0.43	0	1	-0.10	3.2	0.98

Variable	Mean	SD	Min	Max	Skewness	Kurtosis	Normality
Age	35.2	12.5	18	65	0.15	3.2	0.98
Gender	0.55	0.50	0	1	-0.05	3.0	0.99
Marital Status	0.65	0.48	0	1	0.10	3.1	0.99
Education	12.5	2.5	9	16	-0.20	3.3	0.97
Income	45000	15000	20000	80000	0.30	3.4	0.96
Health	0.75	0.43	0	1	-0.10	3.0	0.99
Stress	0.60	0.49	0	1	0.05	3.1	0.99
Depression	0.50	0.50	0	1	-0.05	3.0	0.99
Life Satisfaction	0.70	0.46	0	1	-0.15	3.2	0.98
Resilience	0.65	0.47	0	1	0.00	3.1	0.99
Optimism	0.70	0.45	0	1	-0.10	3.2	0.98
Gratitude	0.60	0.48	0	1	0.05	3.1	0.99
Self-Compassion	0.55	0.49	0	1	-0.05	3.0	0.99
Emotional Regulation	0.65	0.47	0	1	0.00	3.1	0.99
Psychological Well-being	0.75	0.43	0	1	-0.10	3.2	0.98
Life Satisfaction	0.70	0.45	0	1	-0.15	3.2	0.98
Resilience	0.65	0.47	0	1	0.00	3.1	0.99
Optimism	0.70	0.45	0	1	-0.10	3.2	0.98
Gratitude	0.60	0.48	0	1	0.05	3.1	0.99
Self-Compassion	0.55	0.49	0	1	-0.05	3.0	0.99
Emotional Regulation	0.65	0.47	0	1	0.00	3.1	0.99
Psychological Well-being	0.75	0.43	0	1	-0.10	3.2	0.98

Variable	Mean	SD	Min	Max	Skewness	Kurtosis	Normality
Age	35.2	12.5	18	65	0.15	3.2	0.98
Gender	0.55	0.50	0	1	-0.05	3.0	0.99
Marital Status	0.65	0.48	0	1	0.10	3.1	0.99
Education	12.5	2.5	9	16	-0.20	3.3	0.97
Income	45000	15000	20000	80000	0.30	3.4	0.96
Health	0.75	0.43	0	1	-0.10	3.0	0.99
Stress	0.60	0.49	0	1	0.05	3.1	0.99
Depression	0.50	0.50	0	1	-0.05	3.0	0.99
Life Satisfaction	0.70	0.46	0	1	-0.15	3.2	0.98
Resilience	0.65	0.47	0	1	0.00	3.1	0.99
Optimism	0.70	0.45	0	1	-0.10	3.2	0.98
Gratitude	0.60	0.48	0	1	0.05	3.1	0.99
Self-Compassion	0.55	0.49	0	1	-0.05	3.0	0.99
Emotional Regulation	0.65	0.47	0	1	0.00	3.1	0.99
Psychological Well-being	0.75	0.43	0	1	-0.10	3.2	0.98
Life Satisfaction	0.70	0.45	0	1	-0.15	3.2	0.98
Resilience	0.65	0.47	0	1	0.00	3.1	0.99
Optimism	0.70	0.45	0	1	-0.10	3.2	0.98
Gratitude	0.60	0.48	0	1	0.05	3.1	0.99
Self-Compassion	0.55	0.49	0	1	-0.05	3.0	0.99
Emotional Regulation	0.65	0.47	0	1	0.00	3.1	0.99
Psychological Well-being	0.75	0.43	0	1	-0.10	3.2	0.98

Variable	Mean	SD	Min	Max	Skewness	Kurtosis	Normality
Age	35.2	12.5	18	65	0.15	3.2	0.98
Gender	0.55	0.50	0	1	-0.05	3.0	0.99
Marital Status	0.65	0.48	0	1	0.10	3.1	0.99
Education	12.5	2.5	9	16	-0.20	3.3	0.97
Income	45000	15000	20000	80000	0.30	3.4	0.96
Health	0.75	0.43	0	1	-0.10	3.0	0.99
Stress	0.60	0.49	0	1	0.05	3.1	0.99
Depression	0.50	0.50	0	1	-0.05	3.0	0.99
Life Satisfaction	0.70	0.46	0	1	-0.15	3.2	0.98
Resilience	0.65	0.47	0	1	0.00	3.1	0.99
Optimism	0.70	0.45	0	1	-0.10	3.2	0.98
Gratitude	0.60	0.48	0	1	0.05	3.1	0.99
Self-Compassion	0.55	0.49	0	1	-0.05	3.0	0.99
Emotional Regulation	0.65	0.47	0	1	0.00	3.1	0.99
Psychological Well-being	0.75	0.43	0	1	-0.10	3.2	0.98
Life Satisfaction	0.70	0.45	0	1	-0.15	3.2	0.98
Resilience	0.65	0.47	0	1	0.00	3.1	0.99
Optimism	0.70	0.45	0	1	-0.10	3.2	0.98
Gratitude	0.60	0.48	0	1	0.05	3.1	0.99
Self-Compassion	0.55	0.49	0	1	-0.05	3.0	0.99
Emotional Regulation	0.65	0.47	0	1	0.00	3.1	0.99
Psychological Well-being	0.75	0.43	0	1	-0.10	3.2	0.98

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Process for the preparation of derivatives of 4-alkylsulfinylmethylarylenemethanol

the specification of which

- is attached hereto
- was filed on August 27, 1999 as International Patent Application PCT/EP99/06324
- and including all the amendments through the date hereof.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) for which Priority is Claimed:

Federal Republic of Germany, 19840943.5 of September 8, 1998

And I hereby appoint

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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